

Semi-continuous mechanochemical process for biodiesel production under heterogeneous catalysis using calcium diglyceroxide

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Abstract

This work is aimed at the development of a semi-continuous mechanochemical process for biodiesel production and the subsequent valorization of glycerol, its by-product, via its conversion into calcium diglyceroxide using the same mechanochemical reactor. This basic solid catalyzes the methanolysis of vegetable oils. The implementation of a semi-continuous process allows both the preparation of the solid catalyst and the methanolysis process, overcoming the miscibility problems of methanol and oil. Thus, a biodiesel yield higher than 90% is reached using a methanol:oil molar ratio close to stoichiometric value and 1.5 wt.% catalyst, after passing through the reactor with a flow rate between 4 to 45 L/h. This new process for biodiesel production can easily be scaled up and applied to the conversion of used cooking oils, without any significant yield decrease. A cost study was also performed, demonstrating that this is more economical than the conventional batch stirring-based process.

Keywords: *calcium diglyceroxide; biodiesel; heterogeneous catalysis; mechanochemistry; continuous flow; mechanochemical process.*

1. Introduction

The increasing need of fuels for maintaining our living standard has prompted the search of alternatives for traditional fossil fuels, due to the unstable oil price, limited reserves and environmental concerns associated to extraction, production and consumption [1]. In this context, biomass has appeared as a sustainable feedstock for the production of a large variety of biofuels. Among them, bioethanol and biodiesel are the most common liquid biofuels, in terms of production and mature technologies [2,3]. Moreover, the future constrains related to the use of diesel coming from petroleum will require the development of alternatives for transportation, where fuel cells and electricity are called to play an important role. However, the engine compatibility and higher engine wear, higher combustion efficiency, lower sulfur and aromatic contents, lower particulates and carbon monoxide, among other advantages, make attractive biodiesel in comparison with other biofuels [4,5]. Biodiesel comprises long-chain fatty-acid alkyl esters derived from vegetable oils or animal fats, formed by the transesterification/esterification of triglycerides/ free fatty acids with low molecular weight alcohol (mainly, methanol), and can be used either neat (100% biodiesel) or blended with petroleum diesel [6].

In the last two decades, much effort has been paid not only to the development of technologies for decreasing the cost of biodiesel as compared to petro-diesel, but also to the use of non-edible feedstock to avoid any competition with food supply [7,8]. It has been demonstrated that non-edible feedstock can be a sustainable and low cost resource for future biodiesel production [9]. In this context, the use of heterogeneous-catalyzed continuous esterification/transesterification processes for the treatment of non-edible oil seed crops could improve both the environmental impact and energy efficiency of

biodiesel production [10,11]. Different technologies have been proposed for biodiesel production, as alternatives to the conventional batch process using a homogeneous catalyst. In this sense, not only heterogeneous (solid acid and base catalysts) and enzymatic catalysis have received increasing attention, but also non-catalytic technologies based on supercritical processes [12,13]. Moreover, ultrasound-assisted, membrane and reactive distillation technologies, microwave and oscillatory baffled reactors are some examples of innovative process equipment for biodiesel production [14,15].

Solid catalysts are easy to separate from the reaction medium and can potentially be reused for successive catalytic cycles. Much attention has been focused on calcium oxide as solid base catalyst, due to its availability and low cost [16,17]. It can be prepared from calcium carbonate present in minerals (calcite, aragonite) or shells of marine organisms and eggs, by calcination at high temperature. During transesterification process, high methanol:oil molar ratio (6-30) and catalyst loading ranging from 1 to 20 wt.%, together with a reaction temperature of 60-65°C, have been used to attain fatty acid methyl esters (FAME) yields higher than 90% with times longer than 1 h [16]. However, CaO is deactivated by reaction with ambient CO₂ and H₂O, and calcium leaching has been observed (until 0.7 mg of leached CaO per ml of alcoholic phase) [18,19], being more drastic in the presence of free fatty acids in vegetable oils. These soluble species act as homogeneous base catalysts and contribute to the overall catalytic activity, but imply all the drawbacks associated to the use of homogeneous catalysis, such as the requirement of neutralization and washing steps for removing metal species from biodiesel. Moreover, the induction period observed in the kinetic study of this process has been associated to the formation of calcium glyceroxide with glycerol, formed as by-product in the methanolysis of triglycerides [20,21]. This fact has moved different research groups to

synthesize metal glyceroxides as heterogeneous catalysts for biodiesel production [17,22–29], mainly with alkaline (Li, Na and K) and divalent (Ca, Sr, Ba, Zn) metals. Calcium diglyceroxide (CaDG) is the most reported member of this family, and its first synthesis backs to 1910 [30].

The main drawback in methanolysis of vegetable oils is mass transfer between two immiscible phases (oil and methanol), which controls the rate at the initial stage. After this regime, a chemically-controlled (fast) and a final close to equilibrium (slow) regimes have been observed [32]. In this sense, different solutions (magnetic stirrers, ultrasounds, microwave, etc.) have been proposed to reduce the mass transfer limitation. However, these processes increase the overall cost of biodiesel production. Most of the studies focused on transesterification of triglycerides deal with batch processes, suffering of several drawbacks limiting the industrial implementation, such as the need of larger reactor volume, variations in the product quality from batch to batch, among others [33]. Darnoko *et al.* proposed a continuous stirred-tank reactor (CSTR), working with potassium hydroxide as homogenous catalyst, a methanol:oil molar ratio of 6:1, at 60°C, attaining a FAME yield of 85.6% at a residence time of 60 min. However, higher residence times decreased the FAME production rate [34]. A series of CSTRs was employed by Fonseca *et al.* to compensate the loss in productivity caused by shifting from batch to continuous process [33]. They found that using more than five CSTRs decreased the productivity, thus making difficult to reach similar values than those obtained under batch conditions. However, by raising the catalyst concentration facilitated to replace a batch reactor with a single CSTR without losing productivity. More drastic experimental conditions were used by Hsieh *et al.*, who studied the continuous production of biodiesel in a packed-bed reactor with a shell-core structural CaDG/CaCO₃ catalyst, where a FAME yield of 95% was attained at 60°C, with a methanol:oil molar ratio of 30 and a retention

time of 168 min, being the catalyst reused up to 5 catalytic cycles [35]. A Langmuir-Hinshelwood model, involving the adsorption of reactants, surface reaction and product desorption was proposed to explain the catalytic data. The reaction of triglyceride and methanol was the rate-limiting step, since it is slower than those between diglyceride and monoglyceride with methanol.

Mechanochemistry is one of the four sub-disciplines of chemistry established by Matthew Carey Lea at the end of the nineteenth century, although the term was coined by Ostwald, based on the type of energy input, being its history reviewed by James *et al* [38] and Sepelák *et al* [39]. Mechanochemistry deals with chemical and physicochemical transformation of substances in any aggregation state, due to the effect of mechanical energy. The principle is that mechanochemical processes use mechanical energy to activate chemical reactions and structural changes, as well as particle size reduction [40]. In this sense, mechanochemistry helps to overcome diffusional problems as the rate-controlling process. The reaction can proceed with acceptable kinetics without the necessity of raising the reaction temperature, so making feasible to decrease the synthesis temperature and, in most cases, without the use of solvents. Moreover, the application of mechanochemistry can improve the selectivity, favour the homogenization of particle sizes, renovation of surfaces, reduction of calcination temperatures and find out composition out of equilibrium because of the increase of solid solubility between solid solutions and amorphous phases [41].

However, to the best of our knowledge, there is not any process for the preparation of CaDG under a continuous mechanochemical process. In this sense, the production of CaDG has been optimized in order to dispose of pure crystalline phases, characterized by XRD, TG-DTA, N₂ adsorption-desorption at -196°C and SEM. Finally, CaDG has been evaluated as solid base catalyst in the same mechanochemical system, under a semi-

continuous flow, and experimental variables, such as methanol:oil molar ratio, catalyst loading and stirring time after mechanochemical treatment, have been studied to attain the highest FAME yield.

2. Experimental Section

2.1. Reactants

Several calcium sources were evaluated: calcium carbonate (Mikhart 5, La Provencale, 99.10% min), calcium oxide (Calcinor, particle size < 40 µm; >96%), Calcium methoxide (Toplus Inc, 99.6% min) and calcium hydroxide (HX80, Saint Hilaire Industries, 95% min). Glycerol was provided by (99.5% ReactoLab), vegetable oils (Interchimie for Refined Sunflower Oil and Lemman Bio Energie SA for UCO), methanol (Reactolab, 99%) as solvent used for the synthesis of CaDG. A commercial calcium diglyceroxide was supplied by Toplus Inc, China.

2.2. Synthesis of calcium diglyceroxide

Calcium diglyceroxide powders were synthesized by EASYL Company (France), following the method for manufacturing described in their patent [45]. More specifically, CaO and glycerol were mixed in different molar ratios and stirred before pumping to the mechanochemical reactor. This equipment possesses a total volume of chamber of 0.5 L, and contains 55-70% of yttrium-doped zirconia of 0.3-2.0 mm diameter beads; it works with a continuous input flow (between 4 to 150 L/h). After a residence time in the mechanochemical reactor (MCR) of only few minutes, the resulting mixture was collected and stirred until crystal formation. Then, the white solid was washed with different solvents (methanol and/or 2-propanol) to assure the elimination of excess of glycerol and filtered. Finally, it was dried under vacuum to obtain calcium diglyceroxide (CaDG). The resulting solid does not need to be stored under nitrogen to prevent extensive carbonation and hydration.

2.3. Characterization techniques

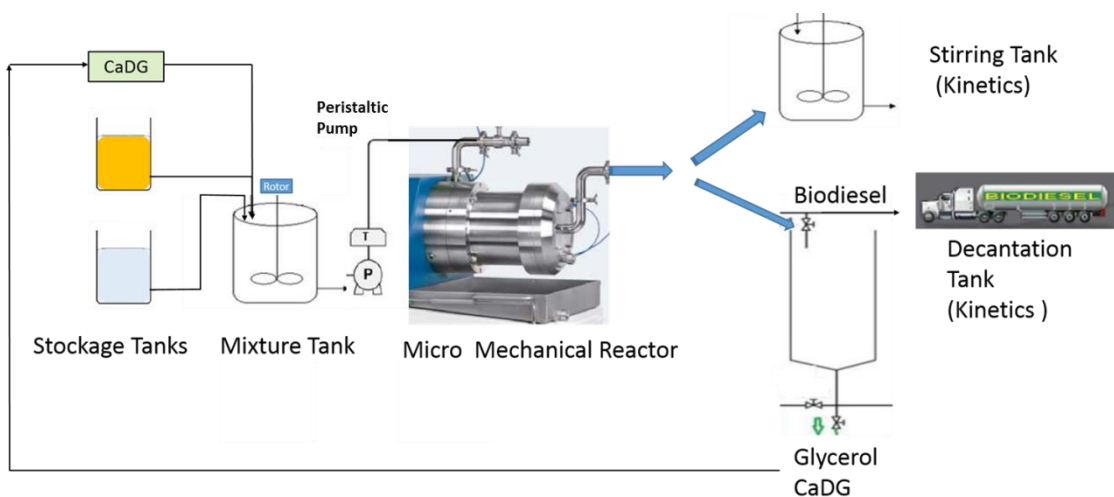
Elemental analyses (C, H, N) were obtained by using a Perkin–Elmer 240 analyzer. Thermogravimetric analysis (TGA) data were recorded on a SDT-Q600 analyzer from TA instruments. Temperature was varied from room temperature to 1000°C, at a heating rate of 10°C·min⁻¹. Measurement was carried out on sample in an open platinum crucible under air flow. Scanning Electron Microscopy (SEM) was carried out using a Zeiss Evo equipped with EDX analysis.

Powder X-ray diffraction patterns for samples were collected on a X'Pert Pro MPD automated diffractometer (PANalytical B.V.), equipped with a Ge (111) primary monochromator (strictly monochromatic Cu K α 1 radiation) and an X'Celerator detector. The overall measurement time was above 1 h per diffractogram to have very good statistic over the 2 θ range of 5-70° with 0.017° step size. XRD patterns were analysed by the Rietveld method, by using X'Pert Highscore Plus version 4.0 software.

2.4. Transesterification of vegetable oil with methanol

Catalytic performance of CaDG was evaluated in the methanolysis of vegetable oils using a mechanochemical reactor under a semi-continuous flow. Refined sunflower oil has an acid degree of 0.2° and a used cooking oil an acidity up to 3° and water content between 300 and 500 ppm. The method followed is described in the patent of the production of fatty acid esters and glycerol at low temperature by EASYL Company (France) [42]. The experiments were performed by mixing vegetable oil and methanol, with a methanol:oil molar ratio close to the stoichiometric value (3:1), in a mixture tank. Then, it was pumped to the mechanochemical reactor (MCR), running under continuous mode. After going through the reactor, the outlet suspension was agitated in a stirring tank, where reaction continues and the kinetics of the transesterification process was studied. Influence of the temperature at the entrance of the MCR and the stirring tank on

the FAME yield was also evaluated. A flow diagram of the semi-continuous system used is shown in Scheme 1. Catalytic data of CaGD using MCR were compared with those obtained with a conventional batch system, based on the use of a 3-neck reactor at laboratory scale (60 ml of total volume). The reaction conditions used in batch were: a methanol:sunflower oil molar ratio of 4:1 and 12:1, catalyst loading of 1.5 to 4 wt.% catalyst respect to oil and temperatures of 50-60° C.



Scheme 1. Flow diagram of the reaction process.

Aliquots for sampling analysis were taken out from the stirring tank, which were centrifuged to separate the catalyst and glycerol from the biodiesel phase. Then, the oily samples were analyzed by gas chromatography (Perkin Elmer Clarus 500) with FID detector, on-column injector and MET-Biodiesel capillary GC column (BP20; 60m \times 0.25mm; SGE Analytical Science). The content in fatty acid methyl esters (FAME) was determined in accordance with the European regulated procedure EN 14103.

Different weight percentages of catalysts were tested, and 1.5 wt. % in relation to the oil mass was enough to ensure a good FAME yield, with a methanol:oil molar ratio of 4:1.

2.5. *Ca diglyceroxide solubility in different medium*

Solubility study was carried out using 0.2 g of CaDG and 5 g of liquid phase, corresponding to 4 wt. % of CaDG. After stirring for different times, solid was separated by microfiltration (filters of 0.45 μm hydrophobic PTFE) and calcium content in the liquid phase was analyzed by ICP-OES.

3. Results and discussion

Recently, much attention is being paid to the use of calcium diglyceroxide as heterogeneous catalyst for biodiesel production. Several studies have demonstrated that CaO reacts *in situ* with glycerol, formed as by product in the transesterification reaction, to form this metal glyceroxide in the reaction medium, being the active phase in the catalytic process [20,21]. This fact could explain the induction period observed when CaO is used, associated to the time required for the formation of CaDG, a more active solid basic catalyst for methanolysis.

The synthesis procedures of CaDG reported in the literature involve several hours of reaction (2-12 h) and temperatures between 50 and 120°C, in the presence of a solvent (usually, methanol) and an excess of glycerol [17,44,45]. Even reported use of ball milling require 5 h for the synthesis [31]. This solid catalyst is a suitable candidate for methanolysis, under heterogeneous conditions, but regarding the synthesis protocol reported in the literature, it is necessary to optimize the process to facilitate its industrial implementation. For this reason, the optimization of the CaDG preparation has been undertaken in the present work. In a preliminary test, influence of the calcium source used for the synthesis of CaDG was evaluated, and several calcium precursors were employed, being their respective diffractograms represented in Figure 1.

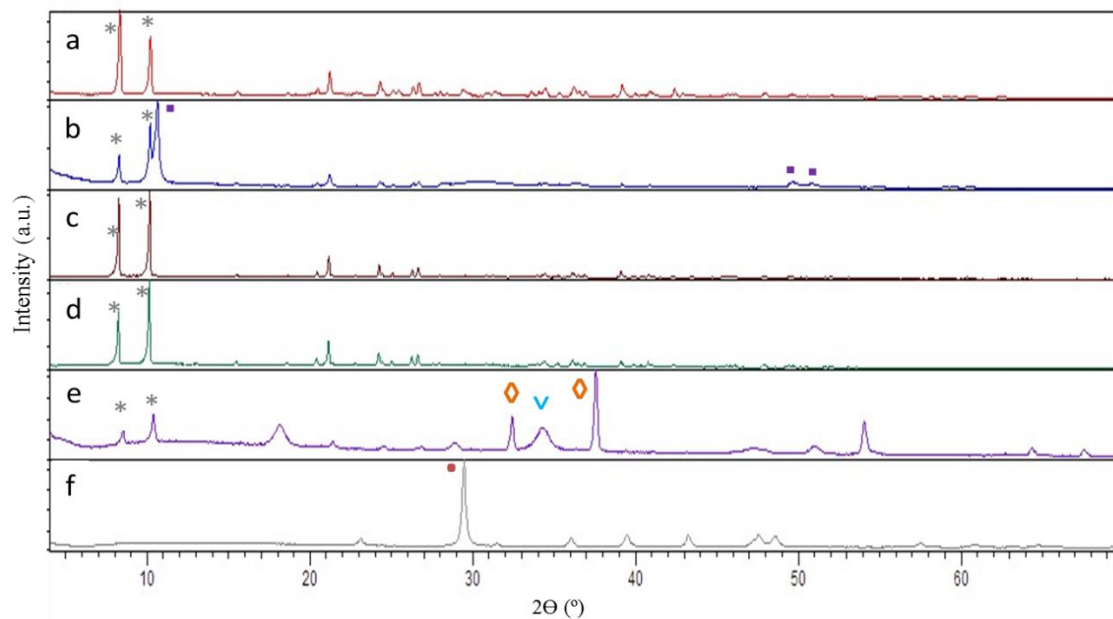


Figure 1. XRD patterns of samples prepared using different calcium sources and phase identification: (a) activated calcium oxide, (b) calcium methoxide, (c) commercial non calcined calcium oxide, (d) milled calcined calcium carbonate, (e) calcium hydroxide and (f) milled calcium carbonate.

Depending on the precursor used, the crystalline phases detected are: $\text{Ca}(\text{OH})_2$ (JCPDS 01-076-0570), cubic CaO (JCPDS 00-004-0777), $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ (JCPDS 00-021-1544), CaCO_3 (JCPDS 00-003-0596) and $\text{C}_2\text{H}_6\text{CaO}_2$ (JCPDS 00-020-1565). A fraction of CaCO_3 remains untransformed when it is used as calcium precursor, even after calcination and milling steps (Fig. 1f). By employing calcium hydroxide as precursor, calcite, calcium hydroxide and diglyceroxide were identified in the respective diffractogram (Fig. 1e). Calcium methoxide does not convert completely to diglyceroxide and even calcium carbonate is detected (Fig. 1b). A commercial calcium oxide, non-thermally activated (frequently used to remove the superficial carbonate formed by contact with air), gives a pure calcium diglyceroxide phase (Fig. 1c). Thus, it is explained because one of the positive effect of the mechanochemical process is the regeneration of

surfaces due to mechanical energy. In addition, the activated calcium oxide and the milled calcined calcium carbonate give calcium diglyceroxide (Fig. 1a and 1d).

Moreover, other experimental parameters, such as stirring time after the mechanochemical treatment, glycerol/Ca molar ratio, and mixture temperature in MCR inlet were optimized (Table 1). The resulting solids were characterized by several physico-chemical techniques, such as X-ray diffraction, elemental analysis, scanning electron microscopy and thermal analysis.

Table 1. Influence of different experimental variables on the formation of CaDG using MCR beads of 0.5 mm of diameter.

Sample	Stirring time (min)	Glycerol/CaO molar ratio	T (°C)	% CaDG (XRD)
1	5	3	25	15.40
2	5	3	50	18.30
3	5	5	25	18.10
4	5	5	50	84.30
5	30	3	25	91.20
6	30	3	50	99.30
7	30	5	25	99.50
8	30	5	50	55.50

XRD patterns (Fig. 2) evidence the presence of several crystalline phases: Ca(OH)_2 , cubic CaO , $\text{Ca(C}_3\text{H}_7\text{O}_3)_2$ and CaCO_3 , depending on the synthesis conditions. However, pure CaDG can be observed in entries 6 and 7 (Fig. 2), more than 99% of CaDG is present with traces of CaCO_3 . For low stirring times, independently of the glycerol/Ca molar ratio and reaction temperature, intense diffraction peaks associated to the presence of calcium oxide were detected in the XRD patterns, together with those of CaDG (entries 1-4).

Moreover, by extending the stirring time up by 10 (high), Ca(OH)_2 was identified in the diffractogram of a sample prepared by using a low molar ratio and reaction temperature (entry 5).

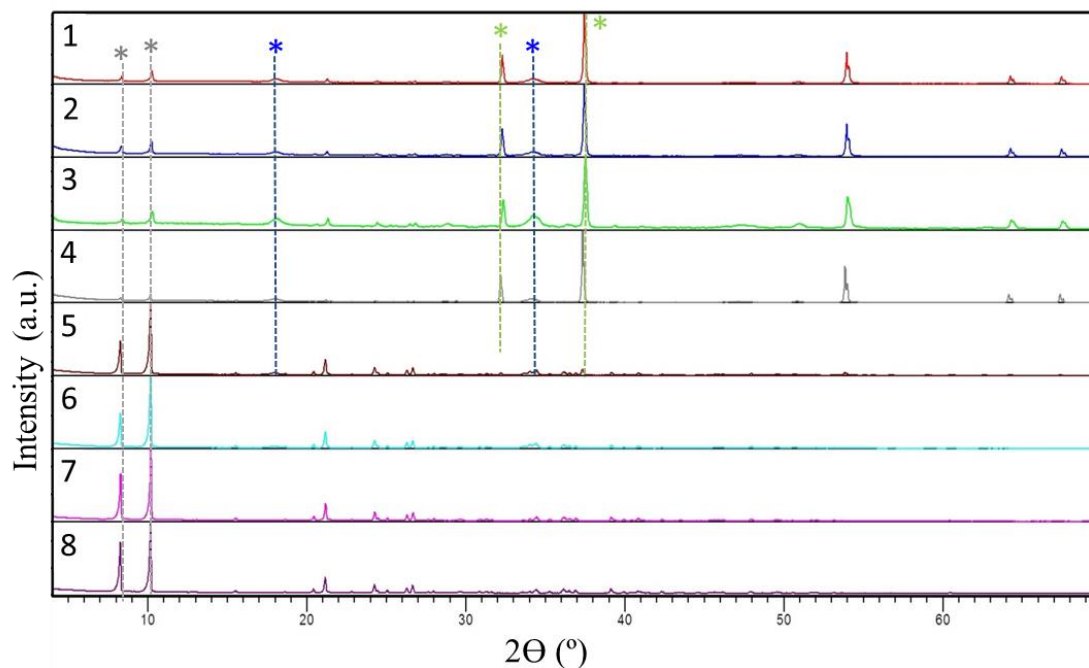


Figure 2. XRD patterns of samples prepared by using experimental conditions gathered in Table 1. The crystalline phases identified are: Ca(OH)_2 (*), CaO (*) and $\text{CaC}_6\text{H}_{14}\text{O}_6$ (*).

The percentage of crystalline CaDG formed was quantified by using the Rietveld method. An initial Rietveld study was carried out with phases of nominal composition, from the structure obtained in the peak identification step. Sample displacement, background, peak profile parameters and the scaling of each phase were refined in order to obtain the best fit and convergence of the refinement (Fig. 3). The XRD diffraction data used for Rietveld study was determined by Leon-Reina et al. that proposed a

mechanism for the transesterification over calcium diglyceroxide, based on the presence of non-protonated O anion at the surface of the structure of calcium diglyceroxide, determined from XRD diffraction data with the Rietveld method [43].

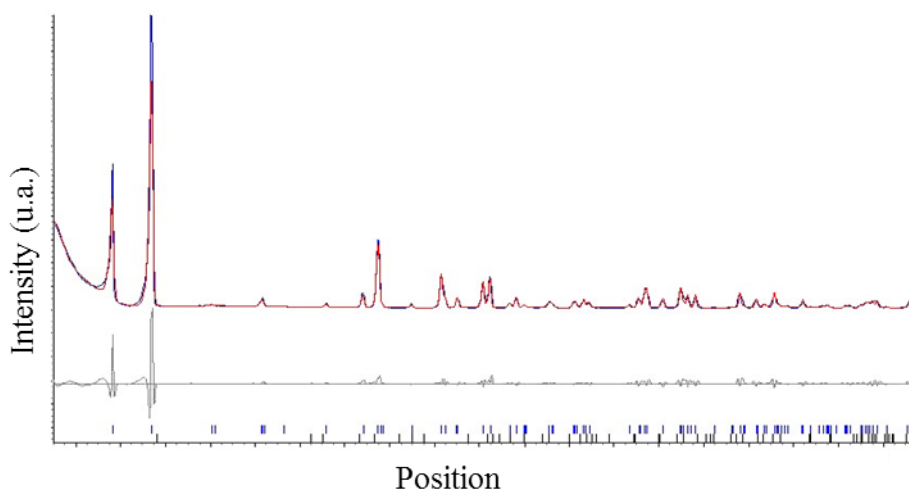


Figure 3. Observed (red), calculated (blue) and difference plots for the final Rietveld refinement of calcium diglyceroxide, $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$, by assuming a non-centrosymmetric space group F222.

For the optimisation, a full factorial experiment of 3 factors with 2 levels (2^3 experiments) was carried out. The factors are: stirring time (STR), glycerol/CaO molar ratio (G/CaO), and temperature (T). The high level (+1) of those factors are: long time, a molar ratio of 5, and 50 °C respectively. The low levels (-1) are: short time, a molar ratio of 3, and 25 °C. The regression analysis of those data allows the estimation of the main effect of each factor on the formation of CaDG, as well as the possible interaction between each pair of factors.

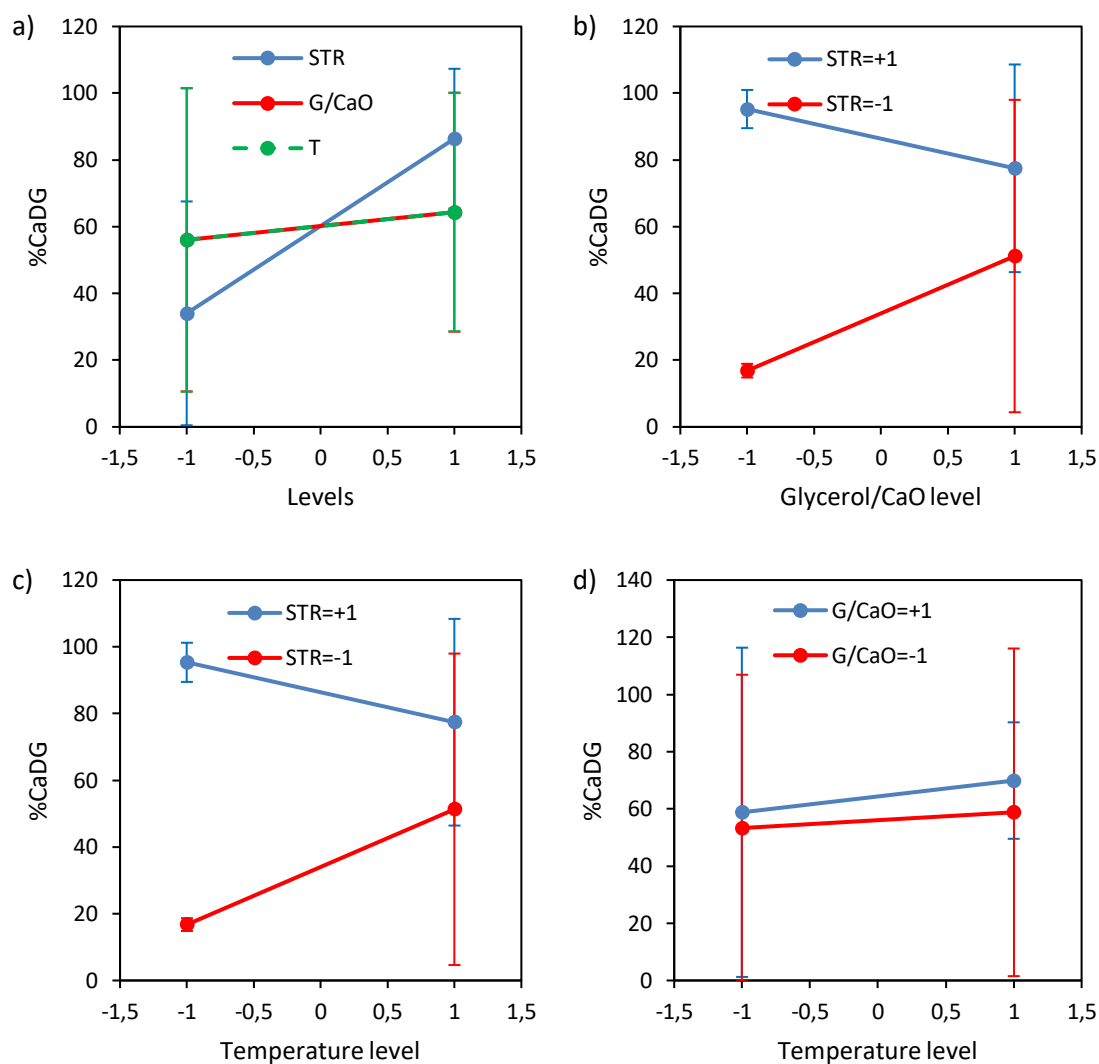


Figure 4. (a) Main effect and interaction plots between (b) STR and G/CaO, (c) STR and T, and (d) G/CaO and T for the factorial experiments of Table 1.

Figure 4 shows the main effect plot and interaction plots that result from the regression analysis. The error bars represent two standard deviations of all the responses considered at each level for the estimation of each particular effect. As can be seen in figure 4a, the stirring time affects significantly the production of CaDG. Figures 4b and 4c, indicate that the effect of the glycerol/CaO molar ratio and of the temperature depend on the level of the stirring time. Finally, no significant interaction is observed between the glycerol/CaO molar ratio and temperature (Figure 4d). The CaDG production can be

estimated well enough from the following equation, which takes into account only the 3 most significant influences indicated above.

$$\begin{aligned} \%CaDG = & 60\% + 26 [STR]_{level} - 13 ([STR]_{level} \times [G/CaO]_{level}) \\ & - 13 ([STR]_{level} \times [T]_{level}) \end{aligned}$$

Therefore, it can be concluded that 30 minutes of stirring time is enough to favor the formation of CaDG; low glycerol/CaO molar ratio and low temperature could be also use without decrease of the percentage of crystalline CaDG. These results are described in the patent of the production of CaDG by Easyl company [46]. Therefore, a pure calcium diglyceroxide was synthesized under continuous flow in the MCR, as XRD pattern has corroborated, with less than 1% of calcium monoglyceroxide presence.

Moreover, several experiments were performed to evaluate if the presence of water in crude glycerol affects the formation of CaDG. The results indicate that the presence of water did not disfavor the formation of CaDG, but, on the contrary, addition of a weight percentage of water between 5 to 15% to glycerol drastically improved the percentage of CaDG in the final product, from 15.4% of CaDG detection without water (Table 1, sample 1) to 82% of CaDG when 10% of water is present in glycerol with the same experimental conditions of sample 1. This was in agreement with the higher reactivity observed as calcium hydroxide was used as calcium precursor for the preparation of CaDG.

The synthesis protocol includes the use of a solvent, such as methanol, in order to reduce the viscosity of the reaction mixture. Different samples were synthesized reducing the methanol content or increasing the temperature (to reduce the viscosity of the mixture). Besides, changing some parameters of the reactor like the size of beads, the patented protocol also allows producing pure CaDG with no solvent. The synthesis

procedures of CaDG reported in the literature involve several hours of reaction (2-12 h) and temperatures between 50 and 120°C, in the presence of a solvent (usually, methanol) and an excess of glycerol [17,44,45]. Recently, Lukic et al have reviewed the methodologies used for the preparation of calcium glyceroxides [31]. Most of them start with a mixture of CaO, methanol and glycerol, with different molar ratios, reaction time and temperature. These authors have proposed the use of a planetary ball mill, and this mechanochemical treatment has allowed synthesizing calcium diglyceroxide but 5 h of milling and addition of methanol as solvent are required.

On the other hand, no precaution must be taken to prevent carbonation and hydration with atmospheric CO₂ and H₂O, during the manipulation of commercial CaO, since an advantage of mechanochemistry is to facilitate the regeneration of solid surfaces [40,47]. Finally, the chemical, textural and morphological properties of CaDG have been confirmed by DTA-TG, Elemental analysis, N₂ sorption and SEM. Micrographs obtained from SEM analysis showed a homogeneous morphology of CaDG particles (Fig. 5).

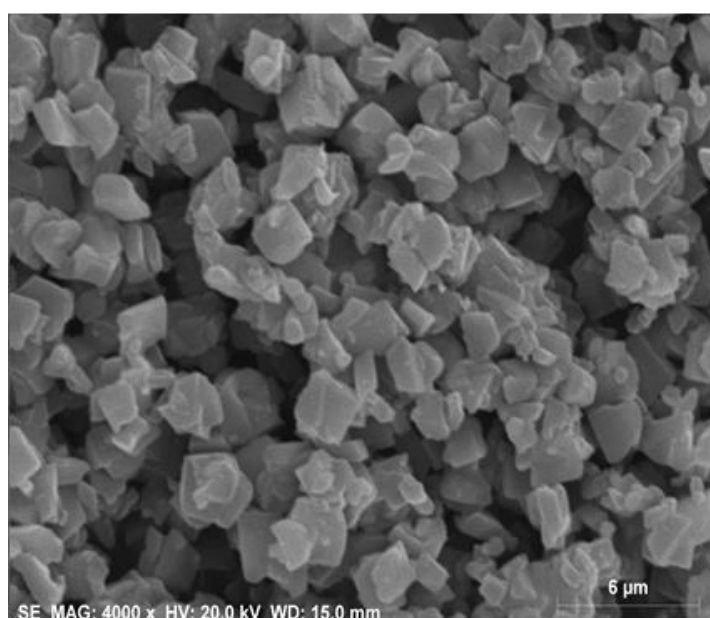
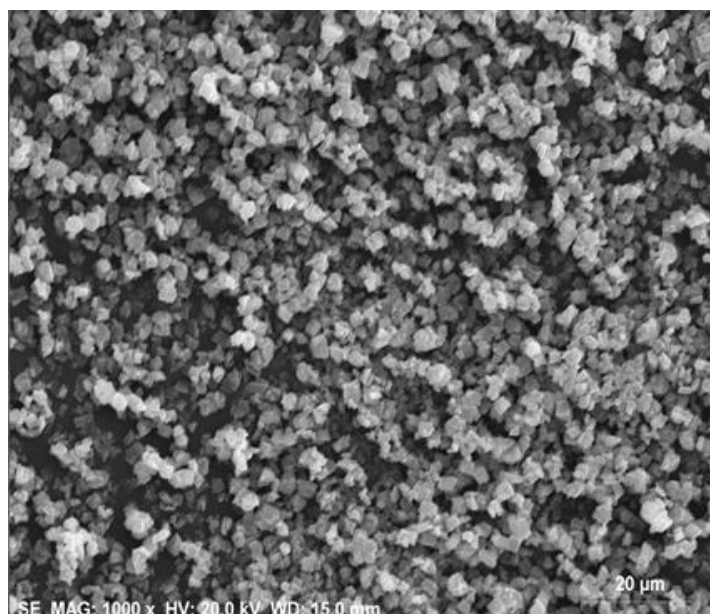


Figure 5. SEM micrographs of calcium diglyceroxide.

Regarding the thermal evolution of CaDG, TG curves exhibit three weight losses (Fig. 6). The two first ones take place at 195 and 405°C and are associated to strong exothermic effects, corresponding to the decomposition of glyceroxide anions to give carbonate. There is a good agreement between the observed mass loss (53.9%) and the calculated value (55.0%) obtained from the reaction: $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2 + 7\text{O}_2 \rightarrow \text{CaCO}_3 + 5\text{CO}_2 + 7\text{H}_2\text{O}$. The third weight loss, between 600 and 740°C, is attributed to the

decarbonation process of calcite to form CaO. Total weight loss corresponding to decomposition and decarbonation is 74.1%, very close to the theoretical value of 74.8%. The composition of CaDG was also confirmed by chemical analysis, with 31.7 wt. % carbon and 6.4 wt. % hydrogen, being the stoichiometric data of 32.4 and 6.3%, respectively.

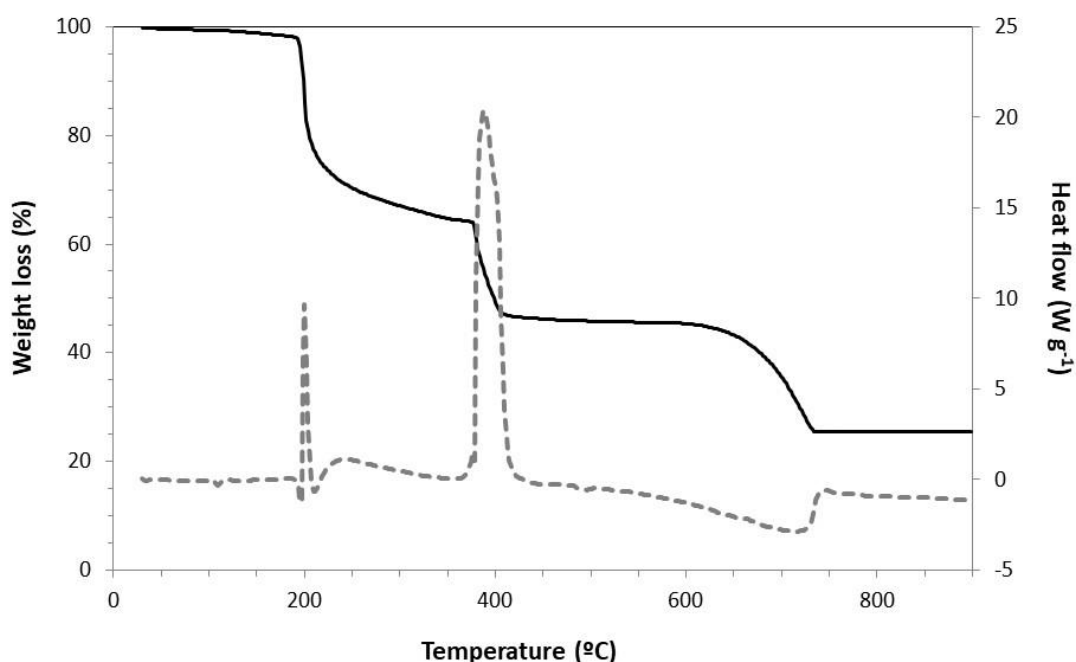


Figure 6. Thermogravimetric (TG) and Differential Thermal Analysis (DTA) of calcium diglycerate.

This material has a specific surface area around $3 \text{ m}^2 \text{ g}^{-1}$, and a pore volume (at $P/P_0 = 0.957$) of $0.0042 \text{ cm}^3 \text{ g}^{-1}$. The average pore diameter (5.7 nm) allows the diffusion of triglyceride molecules toward basic active sites.

Entry	Sample	Area BET m^2/g	V Pore cm^3/g	micropore cm^3/g	Diametre Pore A	%CaDG
5	C26	5.817	0.0267	0.0254	183.4	91
6	C27	3.565	0.0178	0.000024	200.2	99
7	C28	1.575	0.0059	0.000112	151.8	99
BioLeman	BL-1	3.08	0.0042	0.00024	55	99
	BL-2	2.7	0.0039	0.00043	58	99

These textural properties, in terms of BET surface area and average pore diameter, are better in comparison with other metal glyceroxides. Reinoso *et al* synthesized a zinc

glycerolate with a S_{BET} of $1.3 \text{ m}^2 \text{ g}^{-1}$, pore volume of $0.01 \text{ cm}^3 \text{ g}^{-1}$ with pore radius of 2.2 nm [48], whereas CaDG prepared from calcium oxide, obtained after calcination of pulverized lime stone under a helium gas flow at 900°C for 1.5 h, and immersed in glycerol at 60°C , in a nitrogen gas flow of atmospheric pressure, is around $1 \text{ m}^2 \text{ g}^{-1}$ [49].

An important issue in biodiesel production is the solubility of solid catalysts in the reaction medium, since one of the advantages of heterogeneous catalysts is their stability and reusability. However, this drawback has already been reported for most of active catalysts used for biodiesel production [16,50,51]. The solubility of CaDG has been determined in different medium, after 1 and 5 h of stirring (**Fig. 7**), and the results demonstrate that the solubility data can be explained by considering the acid nature of solvents, besides differences in polarity. In this sense, the solubility data of CaDG in oleic acid and water after 1 h are 12.8 and 12.7%, respectively. However, the main difference is found after 5 h, where the solubility in oleic acid is much higher (27%), whereas in water the lixiviated percentage is maintained similar. For biodiesel, only a 2 wt. % is detected after 1 h, which increases until 3.4 wt. % after 5 h; similar values were observed in glycerol and methanol.

These values agree well with those reported by Esipovich *et al.* [51]. It was observed that solubility of CaDG in glycerol rich phase after transesterification, where a high methanol:oil molar ratio was used (9:1), could be associated to the presence of methanol. Data displayed in Figure 10 reveal that solubility of CaDG in methanol is higher than in biodiesel. For this reason, in the present work, a lower methanol:oil molar ratio has been used (4:1) to minimize the possible Ca leaching and to reduce the cost of the elimination of the excess of methanol and calcium from biodiesel. Moreover, Esipovich *et al.* have proposed that CaDG would react with glycerol to form a calcium

polyglyceroxide, more prone to cleavage chain and subsequent formation of soluble low molecular weight fragments [51].

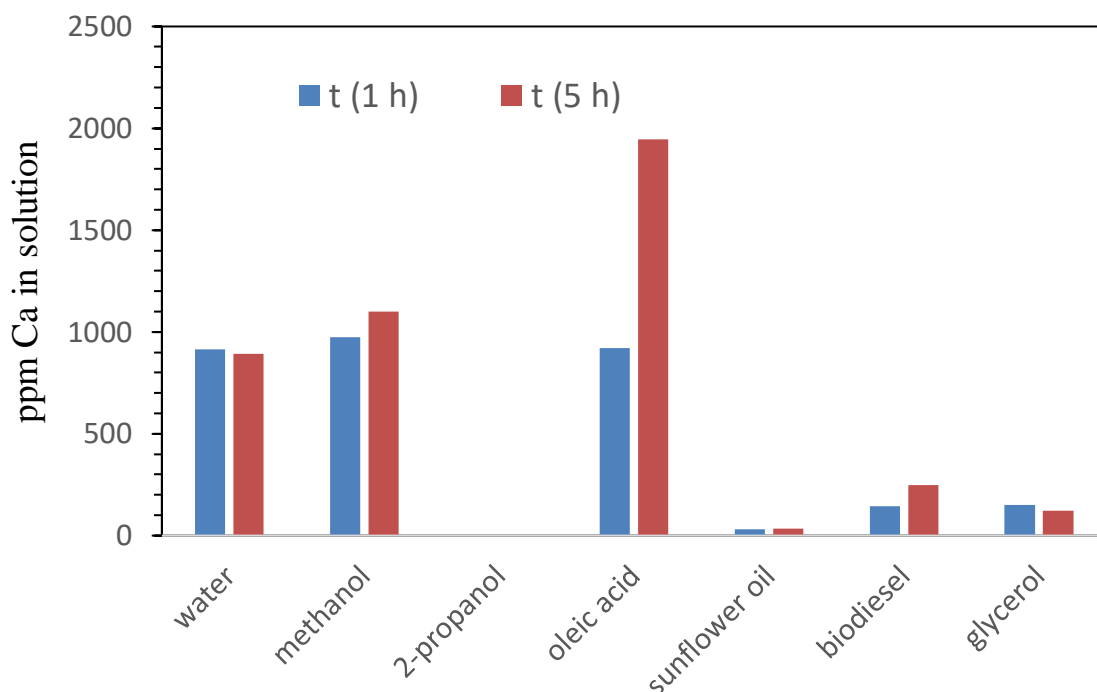


Figure 7. Comparison of solubility of CaDG in different reaction media.

Nevertheless, in the present work, the destruction of the CaDG structure is not an important drawback, since this glycerol rich phase containing calcium species can be used as raw material for the synthesis of crystalline CaDG by mechanosynthesis. It would only be necessary to add the necessary quantity of CaO, and even the presence of methanol is not detrimental for the synthesis of crystalline CaDG.

Calcium diglyceroxide has already been reported as heterogeneous catalyst for biodiesel production. Thus, Gupta *et al.* obtained a maximum biodiesel yield of 93.5%, by using low intensity ultrasonic power of 120 W and 50% duty cycle, with a methanol:oil molar ratio of 9:1, a catalyst loading of 1 wt.% respect to the oil mass, at 60°C, after 30 min [28]. The biodiesel synthesized showed superior properties, according to ASTM

standards, compared to that produced under a batch conventional method. On the other hand, by using a methanol:oil molar ratio of 50:1, a 2 wt.% of CaDG prepared from the method reported by Kouzu *et al.* [24], after 2 h under reflux conditions, a FAME yield of 99% was reached from refined soybean oil [45]. Recently, Lukic *et al.* reported the catalytic performance in biodiesel production of a CaDG prepared by mechanochemical treatment (ball milling). It was found that a triglycerides conversion close to 100% can be attained with a methanol:sunflower oil molar ratio of 10:1, 0.5 wt.% catalyst, at 60°C, after 2 h of reaction [31]. The kinetic model involved the physical effect of CaDG on the reduction of mass transfer resistance, which enhanced the transesterification rate. Moreover, the presence of surface lipophilic CH_x units and basic non-protonated O⁻ anions at the surface of CaDG could explain the high reactivity of this molecule in comparison with CaO, as previously commented [43]. Esipovich *et al.*, with a methanol:oil molar ratio of 9:1 and a reaction temperature of 60°C, attained a 82.6% FAME yield within 2 h with a 1.3 wt.% of CaDG [44]. Concerning the reusability of CaDG, Reyero *et al.* used it for at least 5 reaction cycles without activity loss, working with a methanol:refined sunflower oil molar ratio of 12, a catalyst concentration of 2 wt.%, after 2 h at 60°C, maintaining an oil conversion above 83% [17]. Therefore, the evaluation of the catalytic performance of CaDG for biodiesel production has been carried in batch reactors, at the reflux temperature, with at least methanol:oil molar ratio values of 9:1, and a percentage of catalyst above 1 wt%. However, some discrepancies appear concerning the stability of CaDG in both air (storage conditions) and reaction medium (homogeneous contribution of soluble species to the overall catalytic activity).

Considering previous results about the catalytic performance of calcium diglyceroxide, CaDG prepared by mechanosynthesis has firstly been essayed under batch conditions in order to compare its catalytic performance with data already reported (Table

2). Thus, the catalytic performance of CaDG was compared with a calcined calcium zincate and a commercial CaDG (CaDG_com), at reflux conditions, with a methanol:sunflower oil molar ratio of 12:1 and 4 wt% catalyst at 60°C and 50°C. After 1 h of reaction at 60°C, the order of yield to FAME production was: CaDG (93.2 wt.%) > CaZn (92.4 wt.%) > CaDG_com (85.0 wt.%). At 50°C, when CaDG catalyst is used, 5 h of reaction is needed to achieve similar FAME production (88.7%).

Table 2. Catalytic performance in FAME production of different solid base catalysts with a methanol:sunflower oil molar ratio of 12:1 and 4 wt% catalyst, under batch reflux conditions.

Catalyst	FAME (wt.%)	TG (wt.%)	MG/DG (wt.%)
CaZn ₂ (OH) ₆ .2H ₂ O ^a	92.4	0.8	6.7
CaDG_com	85.0	10.7	4.3
CaDG	93.2	5.4	1.4
CaDG ^b	88.7	3.6	7.7

^a calcined at 400°C; ^b at T= 50°C, after 5 h of reaction time

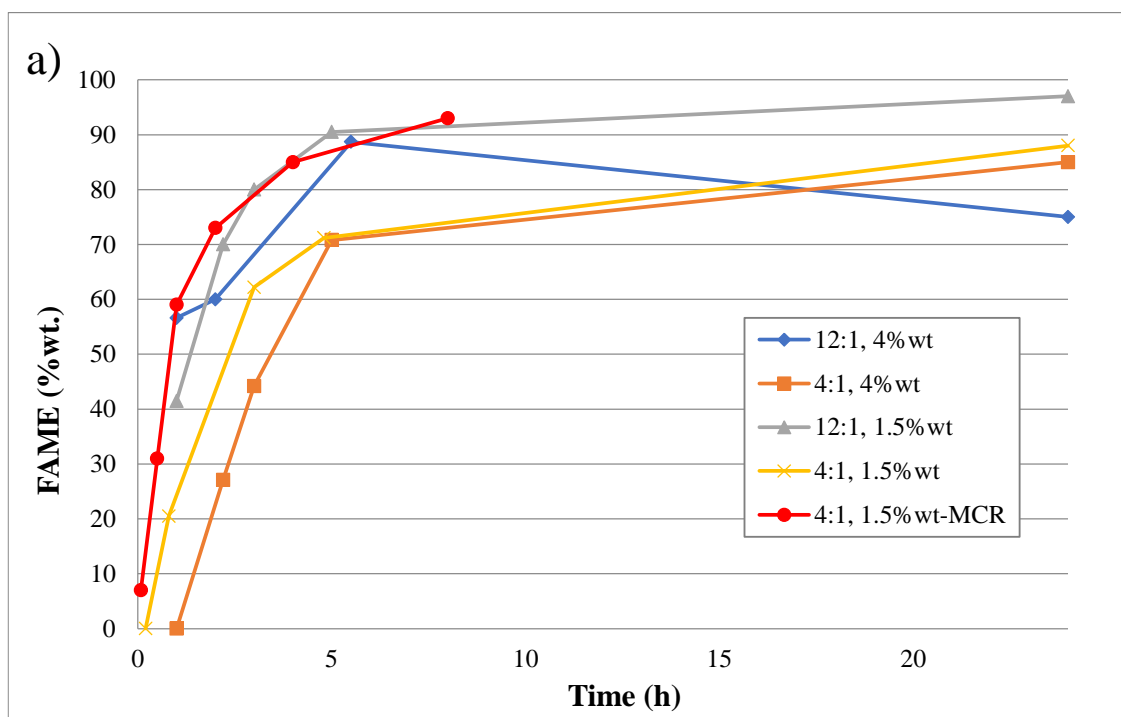
These catalytic results are similar to those previously reported by other research groups, demonstrating that CaDG prepared by a semi-continuous mechanochemical process is a suitable solid base catalyst for biodiesel production. As previously noted, the main drawback in methanolysis of vegetable oils is mass transfer limitations between two immiscible phases (oil and methanol), which controls the rate at the initial stage. Different methodologies (magnetic stirring, ultrasounds and microwaves among others) pursue to overcome this drawback. Moreover, a challenge is to achieve good FAME production

without using high excess of methanol; at lower temperatures and with a moderate quantity of catalyst.

On the other hand, Likozar *et al.* had observed that triglycerides conversion increased by raising the methanol:oil molar ratio from 3 until 4, in a continuous tubular reactor with static mixers (catalyst concentration= 0.8 wt%, total (oil and methanol) volumetric flow rate= 8 mL/min, temperature= 60°C), and then remained almost unchanged after adding more methanol [52], whereas, in batch mode, the positive influence is found up to a value of 7. By using a heterogeneous anion-exchange resin catalysts, the transesterification process is accomplished even for a stoichiometric molar ratio of 3:1, with a FAME purity of almost 100 mol% [53]. However, with a homogeneous catalyst, the total concentration and purity of FAME are higher for a molar ratio of 6:1, although the reaction also proceeds at a ratio of 3:1. Moreover, the raise of the catalyst concentration favoured the conversion to FAME [52].

Taking into account these previous results, the methanol:oil molar ratio is decreased from 12:1 to 4:1 and, at the same time, the weight of catalyst from 4 to 1.5 wt.% in the conventional laboratory scale reactor (3-neck reactor). These experimental values were chosen to compare the catalytic performance of CaDG for biodiesel production from the methanolysis of sunflower oil, by using the MCR equipment. Figure 8 displays the kinetics of the reaction with both systems, at 50°C and room temperature. At 50°C (Fig. 8a), in a conventional reactor with a lower methanol:oil ratio, the FAME production also decreases; on the other hand, a lower quantity of catalyst seems to give higher yield to FAME production. The best performance is reached by using a high methanol:oil ratio and low quantity of catalyst. It can be observed that the use of MCR allows increasing the FAME yield, using a low methanol:oil ratio and low catalyst load (4:1 and 1.5 wt. %, respectively) at 50°C. In general, as expected, a reaction temperature of 50°C led to higher

FAME yields. Thus, after 1 h of reaction time, the main differences are found at 50°C, where the FAME yield increases from 20 until 60 wt. % after passing the reaction mixture by the MCR. At room temperature (Fig. 8b), even after 7 h of reaction time, a FAME yield lower than 40 wt.% is reached.



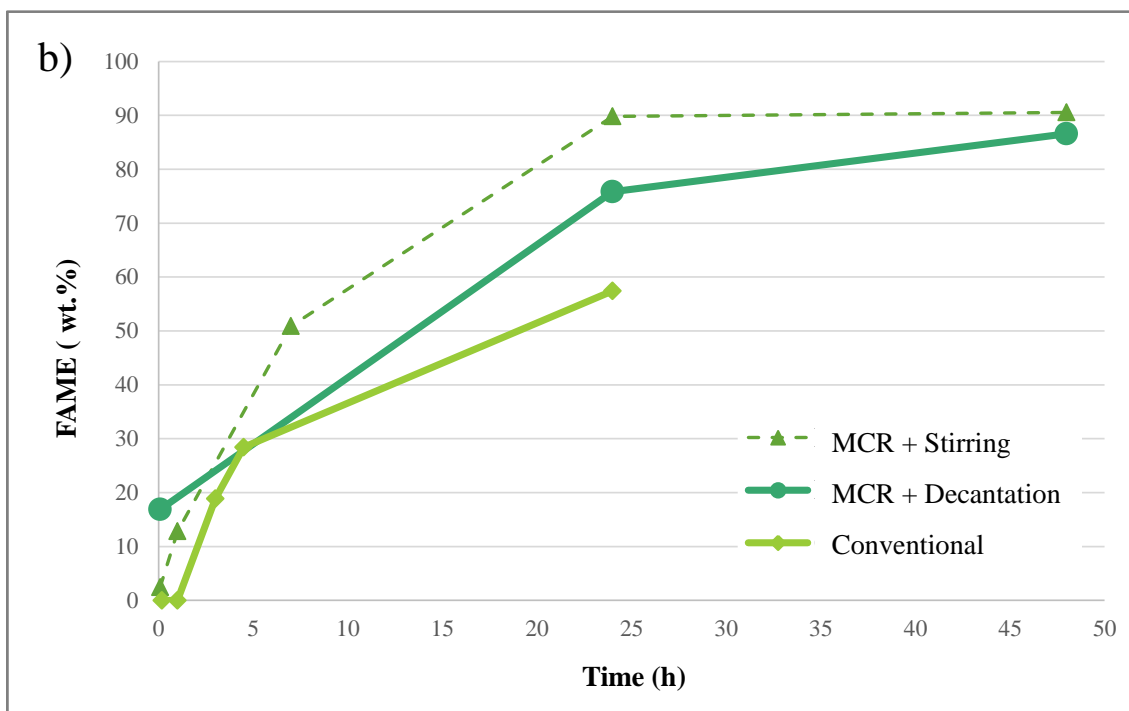


Figure 8. Kinetics of FAME yield under conventional and MCR conditions: a) at 50°C, different methanol:oil ratio and catalyst loading; and b) at room temperature, methanol:oil molar ratio of 4:1 and different post-reaction conditions (MCR reaction and stirring or decantation, and conventional stirring).

At room temperature, the system employing MCR and then a stirring tank showed to be much more efficient than a conventional stirring reactor, since a biodiesel yield higher than 90 wt. % can be obtained after 24 h, whereas only 58 wt.% was achieved under conventional conditions (Fig. 8b). Even in the absence of stirring, just passing the reaction mixture by the MCR and leaving the outlet in a decantation tank, after 48 h a FAME yield close to 90% was attained.

Those results at low temperature and low methanol content are promising if we compared with published results for continuous biodiesel production where higher temperatures (up to 100°C), pressure (1.0 MPa) and smaller flows (around 4 ml/h) are used. A countercurrent trickle-bed reactor packed with CaO was used for continuous

biodiesel production from sunflower oil [36]. However, a higher reaction temperature (100°C) and very low methanol and oil flow rates (3.8 and 4.1 ml/h, respectively) were necessary to attain a FAME yield of 98%. In the reactor, oil droplets released from a thin tube flow downward, and vaporized methanol flowed upward in the bed. Xiao et al. investigated the transesterification in a bench-scale fixed-bed reactor under 1.0 MPa of pressure, with a KF/Hydrotalcite catalyst (cylinder shape), with a liquid hourly space velocity of 0.25-0.76 h⁻¹, CH₃OH:palm oil molar ratio of 9.2-13.7 and temperature of 60-75°C [37]. A FAME yield higher than 95% was maintained through 500 h of continuous operation.

Figure 9 shows the evolution over time of the mechanical energy consumption and of the FAME yield for both systems: conventional and MCR. Regarding energy consumption, the pumping and stirring energy per mass unit processed is the same for both systems, since the only difference between them is the use of the MCR. As can be seen, even though the power required by the WAB may seem high (4 kW), it only works for a very short period, which means an energy consumption of about 0.02 kWh per processed kilogram (vertical separation between striped lines in Fig. 9). This value supposes an increase in mechanical energy of 25% compared to the value consumed at 8 hours of reaction by the conventional system. However, this mechanical energy contribution allows reaching a conversion above 90% at 50°C for a reaction time (8 h), which is 1/3 of the time necessary to get that same conversion in the conventional system. That would mean increasing production by 300%, if the bottleneck was in the reactor. Furthermore, the energy consumption to achieve a conversion above 90% is 2.4 times higher for the conventional than for the MCR system.

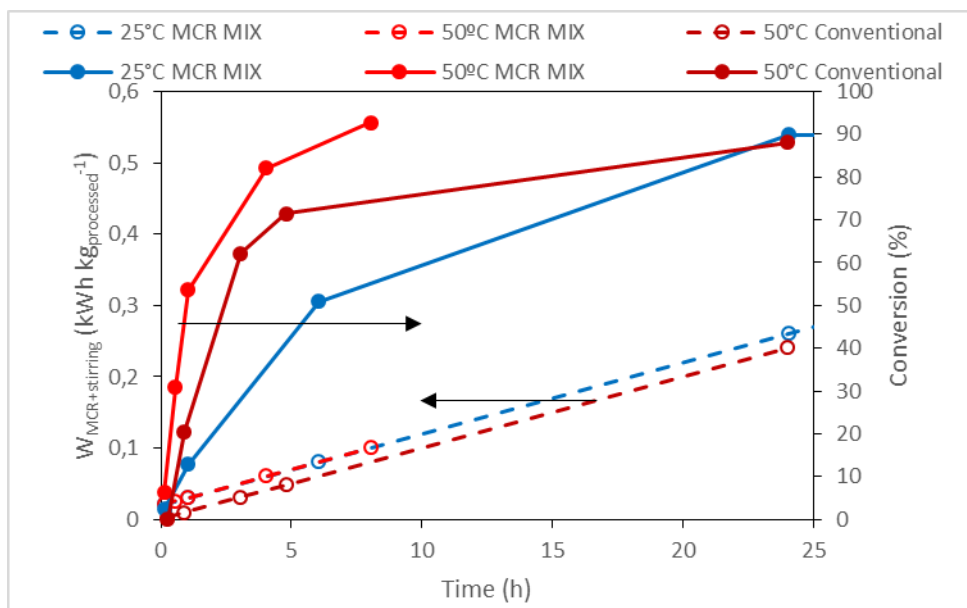


Figure 9. Evolution over time of the mechanical energy consumption and of the FAME yield under conventional and MCR conditions.

Finally, the catalytic performance of the MCR for the treatment of a used cooking oil has also been evaluated. A slightly higher methanol:oil molar ratio was employed (5:1 instead of 4:1), and a lower flow rate (4 L/h). The results have revealed that a similar catalytic activity was observed, except for longer reaction times when a lower FAME yield was observed in the presence of used cooking oil (Figure 10). This could be explained by the neutralisation of basic sites of CaDG by the free fatty acids present in the used oils (until 3°), which could be adsorbed on the solid surface, thus rendering difficult the activation of methanol molecules on active sites.

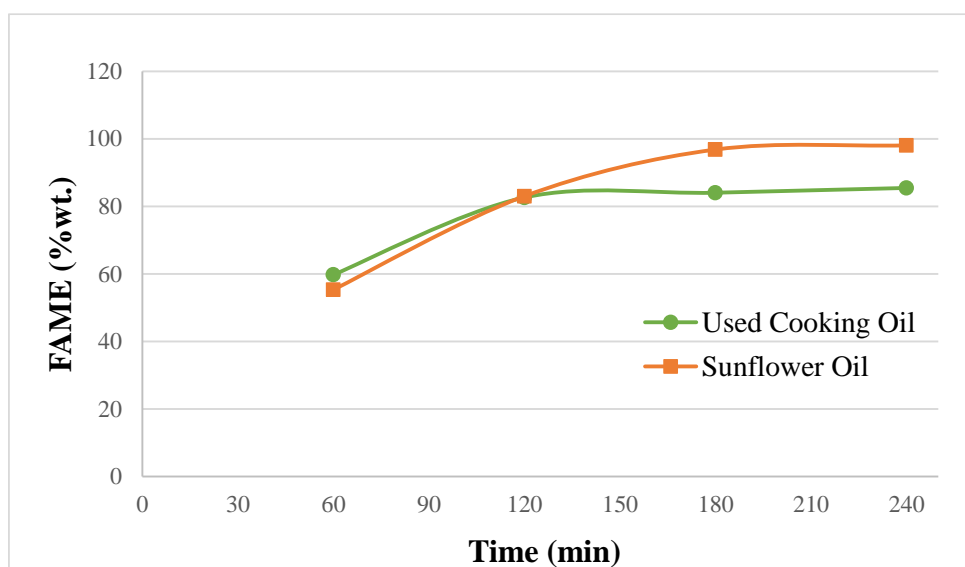


Figure 10. Comparison of FAME production by using sunflower and used cooking oils in the MCR system (Experimental conditions: flow rate= 4 L/h, Temperature= 50°C, methanol:oil molar ratio= 5 and CaDG loading= 1.5 wt.%).

4. Conclusions

In the present work, the potential of a mechanochemical reactor working in a semi-continuous mode for catalyst synthesis and biodiesel production has been proven. In this sense, calcium diglyceroxide catalyst has been synthesized by passing a mixture of CaO and glycerol, without additional solvent, through a mechanochemical reactor and subsequent stirring until the crystalline calcium diglyceroxide can be isolated. This solid base catalyst can efficiently catalyse the transesterification of vegetable oil (sunflower oil and used cooking oil) with methanol. Thus, FAME yield higher than 90% is attained using a methanol:oil molar ratio as low as 4:1, with a 1.5 wt.% CaDG, after passing through the MCR with a flow rate of 45 L/h and subsequent stirring of 4 hours at 50°C, or 24 h at room temperature. This new process for biodiesel production can easily be scaled up, without decreasing the biodiesel yield. The energy consumption study has demonstrated that this semi-continuous process is economically viable, and more favourable than the conventional mechanical-stirring based process. Moreover, glycerol, generated as by-

product in biodiesel production, can be used for the synthesis of the CaDG catalyst, and even the solubilisation of catalyst in glycerol is not a limitation of the process, inasmuch this phase can be used as feedstock for the preparation of catalyst. These results demonstrate that the implementation of a continuous mechanochemical process for flexible-scale biodiesel production is feasible.

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